

PATENT SPECIFICATION

(11) 1 296 136

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DRAWINGS ATTACHED

- (21) Application No. 16013/70 (22) Filed 3 April 1970
 (31) Convention Application No. 813 280 (32) Filed 3 April 1969 in
 (33) United States of America (US)
 (45) Complete Specification published 15 Nov. 1972
 (51) International Classification D06M 15/66 // C08G 47/10
 (52) Index at acceptance
 D1P A18 B5A B5B B5C C2A12A9 C2B2 C2C4 C2C8
 C2C9
 C3T 2 6D4B 6D5 6F2 6J1 6J2D 6J2X 6J4 6J5 6J6 6J8
 7B2 7D2 7E1 7E2 9C



(54) TREATING SYNTHETIC FIBERS WITH ORGANOSILICON COMPOUNDS

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to synthetic organic textile fibers, and, more particularly to treating such fibers to provide a durable, soft, lubricated feel.

It is desired to provide a technique for producing textile fibers having a durable, soft, lubricated feel similar to that possessed by cashmere and other luxury animal fibers such as alpaca and mohair. Some temporary finishes have been used to impart the cashmere feel to fibers, but these finishes are removed by washing.

Somewhat more durable and otherwise satisfactory finishes are the silicones. They implant a pleasant, lubricated feel to synthetic organic fibers. If the silicone is made from an alkyl-hydrogen-chlorosilane so that the polymer will contain some hydrogen groups bonded directly to silicon, the finish will be somewhat durable because cross-linking will occur as the silicon hydrogen groups are hydrolyzed to silanol and these condense to form interchain bridges. But even these silicones will not resist repeated scouring.

Greatly improved scouring resistance is provided by finishes applied as aqueous dispersions of polyepoxides and of siloxanes containing silyl hydrogen atoms. However, these dispersions are not storage-stable, and can produce nonuniform results in commercial practice, because cross-linking reactions commence prior to application especially in the presence of acidic, alkaline, or metallic ion impurities, or when the temperature of the dispersion is elevated.

Improved scouring resistance is also provided by finishes known heretofore made from reactive siloxanes containing free amine groups and a serially-applied fixative containing diisocyanate groups or other groups complementary to amines. However, the serial application process is expensive and complex, imposes requirements of immiscibility between the two solutions or dispersions, and is limited to such mixing of siloxane and fixative as can occur after application.

The pleasant, lubricated feel imparted to synthetic organic fibers by silicone finishes has been attributed to the lower coefficient of friction of fibers coated with the finish with respect to the uncoated fibers. While the synthetic organic fibers coated with the silicone finishes available hitherto have been regarded as more similar to the luxury animal fibers than are the uncoated fibers, a need has been felt for such fibers having a highly durable finish still more closely resembling the characteristics of the luxury animal fibers. An additional need is for a simple process for applying durable silicone finishes onto textile fibers.

The present invention provides a process for treating synthetic organic textile fibers including the application to the fibers of a finishing composition containing (1) a mixture of an aminosiloxane wherein each of the amino groups present carries at least one hydrogen atom and a polyepoxide which has at least 2 epoxy groups per molecule and is not substantially cross-linked or (2) a mixture of liquid epoxysiloxane having an epoxy group content of at least 1% based on the total weight of said epoxysilane and a polyamine having at least 2 amino groups per molecule, each

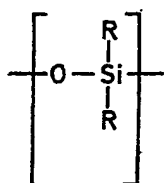
of said amino groups carrying at least one hydrogen atom or (3) a mixture of said epoxysiloxane and said aminosiloxane and subsequent curing of the treated fibers.

In the case of (1) a mixture of 0.05 to 3 parts by weight of the polyepoxide together with 1 part by weight of a liquid aminosiloxane is preferred.

In the case of (2) a mixture of 0.03 to 20 parts by weight of the liquid epoxysiloxane together with 1 part by weight of polyamine wherein each of said amino groups has at least one hydrogen atom and not more than one aromatic ring attached directly to the nitrogen atom is preferred.

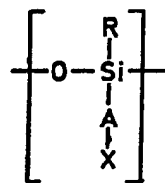
In the case of (3) a mixture of 0.05 to 20 parts by weight of said epoxysiloxane together with 1 part by weight of said aminosiloxane together with 1 part by weight of said aminosiloxane is preferred.

Aminosiloxanes or epoxysiloxanes with the following repeating units are preferred for the inventive finishing process.



I

and



II

In these formulae

R is an alkyl group having 1—4 carbon atoms or an aryl group having 6—9 carbon atoms,

A is an alkylene group having 2 to 5 carbon atoms or an arylene or substituted arylene group having 6 to 10 carbon atoms,

X is —CH—CH_2 or —NH—R' ,



R' being hydrogen, an alkyl group having 1—4 carbon atoms or an aryl group having 6—9 carbon atoms.

In the case of X being —NHR' , R' and A are selected so that not more than one aromatic ring is attached directly to the N atom.

In the case of X being —CH—CH_2 said epoxysiloxanes should, as indicated



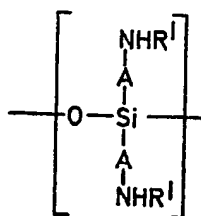
above, have an epoxy group content of at least 1% based on the total weight of said epoxysiloxane.

The preferred aminosiloxanes or epoxy siloxanes contain at least 35 of the above repeating units I and II; at least 2 of these should be II.

The preferred aminosiloxanes for use in this invention are characterized by being liquid and by having one oxygen atom bridging each pair of neighboring silicon atoms, and all other silicon valences being bonded only to carbon atoms. Thus, these aminosiloxanes have no silyl hydrogen atoms. The aminosiloxanes as stated before contain two types of repeating units (I and II) and contain a total of at least 35, preferably 100 to 600, of these repeating units, at least 2, preferably 4 to 20, of which are units II containing the —NHR' group. The degree of polymerization, i.e., the average total number of these two repeating units per molecule, may be as high as 1500 or even higher, provided the aminosiloxane is liquid. The alkyl groups in these aminosiloxanes generally have 1 to 4 carbon atoms and the aryl groups generally have 6 to 9 carbon atoms. Thus, R and R', which may be the same or different, may be, for example, methyl, ethyl, propyl, isopropyl or phenyl.

The repeating units, i.e., the groups I and II usually, but not always, occur randomly in these aminosiloxanes. The aminosiloxanes consist essentially of these two repeating units. Minor amounts of other types of units may be present, provided that the basic properties of the aminosiloxane are not significantly altered, and provided all silicon atoms in the compound are bonded only to oxygen and carbon atoms as described above. Branching units may be incorporated in minor amounts to obtain branched compounds, provided the compounds are liquid. The terminal end groups are usually trialkyl silyl groups, although other terminal end groups, such as hydroxy-alkyl silyl groups or non-silicon-containing groups may be used or there may be no terminal end groups if the molecule is a ring.

If desired, additional amino groups may be present in the second repeating unit (II), for example, by substituting the R group to provide a unit of the formula:



III

Also, the R' group may be replaced with additional —A—NHR' radicals. It is essential that the amino groups be separated from each other and from the silicon atoms by a connecting chain of at least two carbon atoms.

A range of aminosiloxanes having variable weight percentages of amine groups and variable degrees of polymerization are useful. Since aminosiloxanes with a high degree of polymerization are too viscous for easy application, the preferred aminosiloxanes have a degree of polymerization of 100 to 600. The amine content may range from 0.1% to 5% by weight. However, the amine content is from 1% to 3% by weight in the preferred aminosiloxanes i.e., those used in preparing the optimum fiber products having the highest values for Objective Preference Index or OPI (as defined hereinafter, before the Examples) and the greatest similarity to the natural animal fibers.

The polyepoxides used in this invention are characterized by having at least two epoxy groups per molecule. As indicated above these polyepoxides must not be significantly cross-linked, and thus are further characterized by being soluble in any suitable solvent, such as absolute ethanol. This limitation does not imply that the polyepoxide must be soluble in the liquid medium, if any, in which the finishing compound is prepared. A diepoxide such as resorcinol diglycidyl ether is a suitable polyepoxide for use in this invention. Other suitable polyepoxides may be conveniently made by reacting epichlorhydrin with a polyhydroxy compound. One of the preferred polyhydroxy compounds is glycerol. The preparation of polyepoxides from epichlorhydrin and glycerol is described in U.S. Patent 2,872,428.

Other suitable polyhydroxy compounds include bisphenol A [i.e., 2,2-bis(4-hydroxy phenyl)propane]; 4,4'-dihydroxy diphenyl ether; 4,4'-dihydroxy benzophenone; ethylene glycol; diethylene glycol; and propylene glycols. Polyethylene oxide derivatives made by reacting ethylene oxide with polyhydroxy compounds are also suitable for reacting with epichlorhydrin. Thus, glycerol, ethylene glycol and the polyhydroxy aromatic derivatives listed above may first be reacted with from one to twenty moles of ethylene oxide before reacting with epichlorhydrin. Further details of the preparation of suitable polyepoxides are given in U.S. Patent 2,913,356.

When epichlorhydrin reacts with a hydroxy group, it forms an ether. But the epoxy group can react either with a hydroxy group or with another epoxy group so that the resulting products are polymers, rather than simple epoxy ethers. For the purposes of this invention, it is preferable to use low molecular weight polymers or the simple polyepoxy compounds. Polyepoxides with molecular weight of not over 5000 are acceptable, but products in the range up to 1000 are preferred. In most cases, the products used are mixtures of various molecular weights and may contain, and preferably do contain, some monomeric compounds having two or more epoxide groups. Diglycidyl ether itself may be used.

It is preferred that the polyepoxides be water soluble or easily water dispersible for convenience in using, but they can be used in organic solvents, if desired.

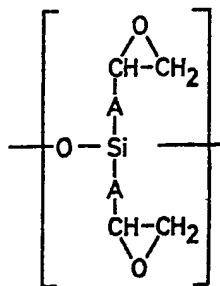
Polymers containing epoxide groups and siloxane groups in the same molecule, as disclosed in U.S. Patent 3,055,774 are also useful in this invention. Disiloxanes such as 1,3-bis-(3-glycidoxypropyl)tetramethyldisiloxane or low molecular weight polysiloxanes containing more than one epoxide group per molecule will yield slick fibers when cross-linked with aminosiloxanes. Epoxy-modified polysiloxanes are particularly useful in combination with the aminosiloxanes and polyamines of this invention. Epoxy-siloxane compounds of this type are characterized by being liquid and by having one oxygen atom bridging each pair of neighboring silicon atoms, and all other silicon valences being bonded only to carbon atoms. Thus, these epoxysiloxanes also have no silyl hydrogen atoms. Also the epoxysiloxanes as stated before contain two types of repeating units I and II and also contain a total of at least 35, preferably

100 to 600, of these repeating units, at least 2, preferably 4 to 20 of which are units II containing the —CH—CH_2 group. The epoxy group content of these epoxysiloxanes



must be at least 1% based on the total weight of the compound. The alkyl groups present in these epoxysiloxanes generally have 1 to 4 carbon atoms, for example, methyl, ethyl, propyl and isopropyl, and the aryl groups generally have 6 to 9 carbon atoms, for example, phenyl. The repeating units, I and II usually also occur randomly in these epoxysiloxanes. The epoxysiloxanes consist essentially of the two repeating units I and II. The limitations concerning the maximum degree of polymerization, possible other repeating units, and terminal end groups previously described with regard to the aminosiloxanes, also apply to these epoxysiloxanes.

If desired, additional epoxy groups may be present in the second repeating unit (II), for example, by substituting the R group to provide a unit of the formula:



IV

Additional epoxy groups may be added, provided the epoxy oxygen atoms are separated from each other and from silicon atoms by a connecting chain of at least two carbon atoms.

It is preferred that the epoxy siloxanes be water soluble or easily water dispersible for convenience in using, but they can be used in organic solvents or without solvents, if desired.

The epoxysiloxanes may be used in conjunction with the aminosiloxanes described above or the amine compounds described below, to provide results similar to that obtained with a combination of the aminosiloxane and the described epoxy compound. In all cases improved and useful slickness is obtained in the treated fiber as compared with the untreated fiber. However, only when an aminosiloxane is employed as one ingredient do the fibers exhibit marked similarity to the natural luxury animal fibers, accompanied by high values for the Objective Preference Index.

The polyamine compounds that are used in combination with the epoxysiloxanes in accordance with this invention are characterized by containing primary and/or secondary amino groups and having at least two amino groups per molecule. Examples of suitable amines are ethylene diamine, diethylene triamine, and other alkylene and arylene polyamines, N-alkyl alkylene diamines, N-alkyl arylene diamines, diazines such as piperazine(hexahydropyrazine), aminopiperidines such as 2-aminohexahydropyridine. Primary amines are preferred over secondary amines. Tertiary amines are not operable for use in this invention.

In mixtures of epoxysiloxanes and aminosiloxanes alone, the ratio of epoxy-siloxane to aminosiloxane may vary from about 0.05:1 to about 20:1 by weight, but in mixtures of aminosiloxanes with epoxy compounds other than epoxysiloxanes and in mixtures of epoxysiloxanes with amino compounds other than aminosiloxanes, the ratio of the non-siloxane compounds to the siloxane compounds may vary from about 0.05:1 to about 3:1 by weight, with the preferred ratios in all cases varying according to the specific compounds employed. The amino-siloxane-epoxy composition may be prepared as solution in an organic solvent or, more preferably, as an aqueous dispersion. The concentration of the composition in such a solution or dispersion may vary over a wide range, but a siloxane concentration of 2% to 20% by weight is generally adequate. Similarly, the amount of amino-siloxane-epoxy composition that is applied onto the fibers may vary over a wide range, depending upon the particular effect that is desired to be obtained. Generally about 0.1% to 3% of siloxane, based on the dry weight of the fibers, will be adequate, and about 1.0% to 2% siloxane is usually preferred.

It is preferred that the amine-containing compound and the epoxide-containing compound be mixed only a short time before using. The aminosiloxane or epoxy-

siloxane can be dispersed in water by means of cationic or nonionic surface active agents. Suitable cation active agents are stearyldimethylbenzyl ammonium chloride, stearylcolamino(formyl)methyl pyridinium chloride, and cetyltrimethyl ammonium chloride. A suitable nonionic type is an ether of nonylphenol and a polyalkylene glycol. After the components are dispersed and mixed, the resulting composition is applied to the fibers, preferably at room temperature, inasmuch as heating tends to cause premature cross-linking and precipitation of the polymers.

When a solvent solution of finishing composition is desired, the siloxane-containing compound is usually just dissolved in a suitable solvent such as methylene chloride or other chlorinated hydrocarbon or ethanol and then the epoxy compound is added. The organic solvent solution can then be applied to the fibers, or it may be added to water containing an emulsifying agent to form an emulsion of the siloxane and the polyepoxide, and the resulting emulsion can be applied to the fibers. The product can also be made by applying solutions or dispersions of the two ingredients to the fiber in serial manner and then curing them together on the fiber; although for economic reasons and optimum product uniformity the ingredients are generally applied together in solution or dispersion in accordance with the process of the invention.

The product can also be made using salts of the aminosiloxane formed by mixing the aminosiloxane with a sufficient quantity of a relatively volatile acid to neutralize all the amino groups. Neutralization of the aminosiloxane retards reaction between it and the polyepoxide. This retardation is particularly useful if it is desired to expose the coated fibers to elevated temperatures, e.g., during crimping, before evaporating dispersing medium or solvent and curing the composition. Removal of the volatile acid during evaporation and curing regenerates the aminosiloxane which then reacts readily with the polyepoxide.

All synthetic organic textile fibers, such as fibers of acrylonitrile polymers, polyamides or polyesters, may be treated in accordance with this invention. The treated fibers comprise a further feature of the invention. Fibers of acrylonitrile polymers, including homopolymers and copolymers, are especially benefited by this invention. Suitable polyamide fibers for treatment in accordance with this invention are fibers of poly(hexamethylene adipamide), polycaprolactam, and polyamides from bis(4-aminocyclohexyl)-methane and dicarboxylic acids containing 6 to 16 carbon atoms such as poly(methylene-di-1,4-cyclohexylene dodecanediamide).

The composition used in this invention may be applied to fibers in the form of a tow or staple fibers, to filaments or spun yarn or even to finished fabric. However, it is the prime object of the present invention to treat the fiber in the form of tow or staple where it would be most economical and where the application can best be controlled to give uniform results. The treated tow or rope may conveniently be cut into staple after impregnation and before curing.

After the finishing composition is applied to the fibers, any dispersing medium or solvent is evaporated and the composition is cured by subjection to elevated temperatures, usually within the range of 110 to 160° C. for about 15 to 40 minutes. Lower temperatures may be used, at a sacrifice of curing time, and in some instances higher temperatures may even be used. In every case the temperature should be low enough to prevent the fiber substrate from being deleteriously affected.

When this invention is used to treat fibers in the form of tow, it has been found that best results are obtained if the tow to be treated is free of oily finishes. The finishing composition made from the free amine is preferably not applied before hot crimping because the heat would cause premature polymerization of the mixture. The fibers may be lubricated with a textile finish before crimping, if desired. After crimping, the finishing composition may be applied without removing the crimp.

After treatment in accordance with this invention, fibers have a soft, slick finish that is remarkably durable. This finish will not only withstand repeated wearing and washing or dry cleaning of garments made from treated fibers, but will withstand the rigorous scouring and dyeing operations that are employed in the numerous steps involved in converting tow into staple, then into yarn, and finally into fabrics and garments. Moreover, it is surprising that this finish does not interfere with ordinary dyeing operations. These remarkable properties make this invention particularly useful for treating tow.

In addition to providing a durable, soft and lubricated feel to fibers, the process of this invention imparts other remarkable properties to fibers. For example, fibers finished by the process of this invention yield fabrics which have less tendency to form pills on the surface. Also, the fabrics do not glaze as badly as do fabrics from untreated fibers. Glazing is a condition where fibers are flattened and shaped into a plane surface so that the fabrics have a "shine". It is caused by hot pressing which

fixes the fibers in place and they become slightly adherent to each other. It is believed that the finishing composition decreases glazing by acting as a release agent, keeping the fibers from sticking together and from being fixed in a plane surface. This freedom of motion is also believed responsible for some improvement in wrinkle resistance imparted by these agents to the fabric. The silicones alone produce similar benefits, but only temporarily. The effects are largely lost after one or two scourings or dry cleanings.

The fiber finishes obtained in accordance with this invention are more durable than the finishes obtained with the aminosiloxane or the epoxysiloxanes when used alone. The aminosiloxane when used alone remains fluid and tacky, but when combined on the fiber with a polyepoxide or with an epoxysiloxane it gives a soft, dry, slick hand to fibers and to fabrics made from the fibers. Similar synergistic results are obtained when the epoxysiloxane is reacted with a polyamine.

All of the fiber finishes provided by the process of this invention are highly durable on the fiber and impart a pleasant, lubricated feel to the fiber, as contrasted with the corresponding untreated fiber. Moreover, it has unexpectedly been found that synthetic organic fibers bearing an aminosiloxane-epoxy (polyepoxide or epoxysiloxane) composition exhibit frictional characteristics over a range of measuring speeds highly analogous to the frictional characteristics of luxury animal fibers. Garments made of the fibers coated with the aminosiloxane-epoxy composition have a slick, soft feel markedly resembling the feel of garments made of luxury animal fibers. Surprisingly, the luxurious feel of garments of these fibers is long-lasting and persists throughout many laundering or dry cleaning cycles to which the garment is subjected during normal wear.

The character of the desirable frictional behaviour of the synthetic organic fibers bearing the aminosiloxane-epoxy composition will be more clearly understood by reference to the accompanying figures, which are plots of the friction coefficients, measured over a wide range of sliding speeds, of various fibers. Referring to Figure 1, the coefficient of friction vs. sliding speed of an acrylonitrile terpolymer coated with an aminosiloxane-epoxy composition as described in Example V is plotted in the manner described hereinafter. It will be observed that the coefficient of friction curve of this fiber of the present invention is characterized by a relatively low initial coefficient of friction; the curve dips slightly lower to a minimum (F_{min}) as the sliding speed is increased, and then rises sharply and progressively as the sliding speed is increased to 100 cm./sec. (F_{100}). This characteristic curve is observed with other fibers of this invention having an aminosiloxane-epoxy composition coating.

It has been discovered that natural luxury animal fibers also have similar characteristic curves. Referring to Figure 2, it will be seen that with alpaca and mohair, for example, the coefficient of friction is initially relatively low, and dips slightly lower to a minimum as the sliding speed increases, and then rises sharply and progressively as the sliding speed is increased to 100 cm./sec. Thus the coefficient of friction curve for the fiber of this invention (the curve shown in Figure 2 is the same as shown in Figure 1) has the same characteristics as the natural luxury fibers. By contrast, the coefficient of friction of an untreated acrylonitrile polymer fiber shows a sharp progressive decrease as the sliding speed is increased, followed by only a modest rise, and at 100 cm./sec., it is substantially lower than the initial value. The acrylonitrile polymer fibers having other silicone-epoxy coatings (also described in Example V) also have markedly different coefficient of friction curves as shown in Figure 2.

Thus, Figure 2 graphically illustrates the phenomenon that the acrylonitrile polymer fibers of the present invention coated with an aminosiloxane-epoxy composition feel to the human hand remarkably similar to the natural luxury fibers. Other silicone-epoxy compositions, while providing considerable improvement in slickness compared to unmodified acrylonitrile polymer fibers, do not realistically simulate the feel of the natural luxury fibers. Figure 3 illustrates the characteristic coefficient of friction curve of a polyethylene-terephthalate fiber treated in accordance with this invention as described in Example IX.

Plots of the coefficient of friction of fibers, with respect to the sliding speed at which the measurement is made, are prepared as follows, except where otherwise specified. The test is carried out on staple fibers, and if the sample is submitted as a tow it is first cut to staple fibers, preferably about 3 inches in length. A 2.0 g. sample of the staple fibers is carded by hand until the fibers are roughly parallel and lie as a sheet on one of the sample cards. About 0.8 g. of this card "web" is laid onto the surface of two-inch wide, two-sided pressure-sensitive tape, wrapped around a two-inch diameter cardboard tube. Fibers are distributed axially around the tube to

provide an even coverage of the tape. Both ends of the fiber-covered tape are then wrapped with narrow masking tape to anchor them more firmly.

An 0.25 g. portion of the carded fibers is then applied evenly to the surface of a 1" x 9" strip of one-sided pressure-sensitive plastic tape. Since the tape is longer than the fibers, it is necessary to apply them in overlapping sheets, similar to application of shingles on a roof. The last half inch of each end of the tape is not covered with fibers and is folded over to provide a reinforced anchorage for attachment to the apparatus to measure friction.

The staple-covered tape is draped over the staple-covered cylinder to provide 180° contact. The fibers at the interface contact each other at approximately right angles. One end of the tape is attached to a force-recording cell and the other is attached to a static load of 30 g. The cylinder is then rotated so that its circumference turns in the direction from the force-recording cell to the static load. Friction force data are recorded at sliding speeds ranging from 1.6×10^{-2} to 100 cm./sec. depending on the rotating speed of the cylinder.

Friction coefficients are calculated using the following equation:

$$T_2/T_1 = e^{\theta}$$

T_2 = Frictional force from strain gauge.

T_1 = Weight attached to staple-covered tape.

θ = Contact angle of tape with cylinder in radians = 3.14

F = Friction coefficient.

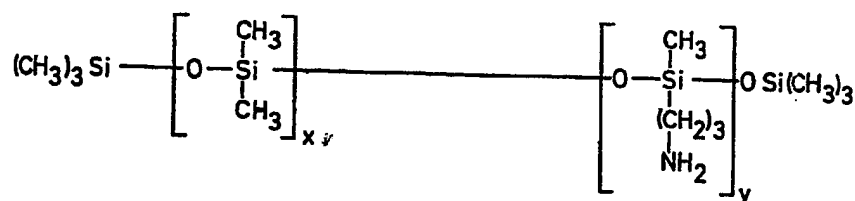
A curve such as that shown in Figure 1 is plotted and a mathematical ratio is calculated. This ratio, called the "Objective Preference Index" and abbreviated "OPI" is obtained by dividing the difference between the value of the coefficient of friction at 100 cm/sec. (F_{100}) and the value of the coefficient of friction at the minimum point in the curve (F_{min}) by the coefficient of friction at the minimum point (F_{min}) in accordance with the equation:

$$OPI = \frac{F_{100} - F_{min}}{F_{min}}$$

The present invention provides not only excellent fiber properties, but also marked process advantages. The components are intimately mixed before application, so that uniformity of the cured finish is promoted and only a single application is made. Only two components are required to be mixed together, which provides a simple mixing procedure. The aqueous dispersions of each component are relatively storage-stable, which promotes uniform results in commercial practice. Finally, the curing step takes place rapidly and smoothly.

Example I

Eight parts of an aminosiloxane having the formula:

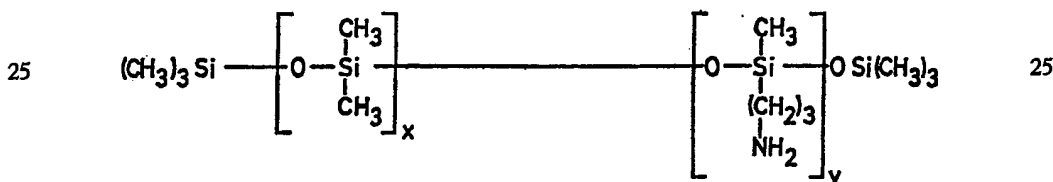


and having a degree of polymerization (i.e., the value of $x + y$ which is abbreviated hereinafter as "DP") of 500 and an NH_2 content of 0.2% (aminosiloxane supplied by Union Carbide Corp., designated Y5230) is stirred with 391 parts of methylene chloride, and 1.2 parts of a polyepoxide is added. This polyepoxide is a liquid mixture of linear and moderately branched propylene ether polymers containing hydroxyl groups, chloromethyl groups, and an average of at least two epoxy groups per molecule; it is a condensation product of glycerine and epichlorhydrin; it has a pale yellow color; it has a viscosity of 90 to 150 centipoises at 25° C. (polyepoxide supplied by the Shell Chemical Corp., designated "Eponite" 100—"Eponite" is a registered Trade Mark). The resulting solution is used to treat 52.2 parts of an acid-dyeable staple fiber made by dry spinning from solution in dimethyl formamide a polymer of 92.2 parts acrylonitrile, 5.4 parts methyl vinyl pyridine, and 2.4 parts methyl

acrylate. The treatment consists of dipping the staple into the solution, removing and squeezing to 100% pickup of the solution (i.e., the fibers picked up an amount of composition equal to their own dry weight). This staple is then heated for 20 minutes at 70° C. and then 30 minutes at 130° C. to fix the finish on the fiber. The staple is next carded into a sliver. This sliver is combined with 22.8 parts of an untreated, acid-dyeable, high-shrinkage sliver made from a polymer of 89.6 parts acrylonitrile, 4.7 parts methyl vinyl pyridine and 5.7 parts methylacrylate. The combined slivers are spun into a 6/1cc (886 denier) yarn having 5Z turns per inch twist (1.97 turns per cm.). The yarn is dyed in skein form for 1.75 hours at the boil at a pH of 2.5 with Pontacyl Brilliant Blue RR (Dye Index No. 42735). For each 100 parts of fiber, 2 parts of dyestuff, 3 parts sodium sulfate and 0.5 part of leveling salt are dissolved in 200 parts water and the pH adjusted to 2.5 with sulfuric acid. Dyeing is 1 hour 45 minutes at the boil. After dyeing, the fiber is scoured at 70° C. using a sodium alcohol sulfate detergent. It is rinsed and dried. The boiling causes shrinking of the high shrinkage fiber yielding a bulky yarn and causes the treated fibers to come to the surface. This yarn is next knit into a novelty construction on a Passap Duomatic (registered Trade Mark) flat bed knitting machine and tested for slickness before and after scouring and before and after mechanical, dry abrasion. The slickness is retained through all these operations; that is, opening and carding of the staple, twisting and drafting of the sliver, skeining and dyeing of the yarn, knitting, scouring and abrading of the fabric.

Example II

Eight parts of a trimethyl silyl-end-capped, random copolymer of dimethyl siloxane and methylaminopropylsiloxane which is described by the formula:



having a DP of 200 and an NH₂ content of 1.82% (aminosiloxane supplied by Union Carbide Corp., designated Y 5455) is added to 391 parts absolute ethanol with stirring and 1.2 parts polyepoxide ("Eponite" 100 as described in Example I) is added. Fifty parts of a basic-dyeable staple fiber spun from a polymer of 95.8 parts acrylonitrile and 4.2 parts sodium styrenesulfonate are dipped into the siloxane-epoxide solution then pressed to remove excess solution, leaving 100% of solution on the fiber. The fiber is dried and heated 35 minutes at 130° C. to cause interaction of the aminosiloxane and the epoxide on the fiber. The treated fiber is next carded and formed into sliver A.

A bicomponent staple fiber with a homopolymer of acrylonitrile on one side and making up 75% of the filament, and a copolymer of 95 parts acrylonitrile and 5 parts sodium styrenesulfonate on the other side and making up 25% of the filament is slickened in the same manner except from methylene chloride solution and converted into sliver B. Sliver A and sliver B are blended on a pin drafter and spun into a 10/1cc (531 denier) yarn with 7.1Z turns per inch (2.8 turns per cm.) twist. This yarn is knit into a jersey fabric having 16 courses per inch (6.3 courses per cm.) and the fabric is scoured and then dyed at the boil at a pH of 4.5. The resulting fabric is soft and slick, and the slickness is not destroyed by hand abrasion. The bicomponent fiber crimps during the dyeing and results in a bulky yarn.

Example III

The example demonstrates the use of a combination of an epoxysiloxane and a diamine as a fiber finish.

Eight parts of epoxysiloxane having 5% epoxy group and a viscosity of 700 CSTKS at 25° C and 1.6 parts of 1,6-diamino-hexane are dissolved in 390 parts of absolute ethanol. One hundred parts of the basic-dyeable staple fiber of Example II are dipped into this solution and the excess solution squeezed out to leave 100% wet pickup. The fiber is then cured 30 minutes at 130° C. and then spun into a 10/cc (531 denier) 7.1Z turns per inch (2.8 turns per cm.) yarn. This yarn is knit into a 16 stitch/inch (6.3 stitch/cm.) jersey fabric and dyed at a pH of 4.5 with basic cationic

dyes. After scouring and drying, this fabric has a soft, slick hand which is retained through many launderings and repeated abrasions.

Example IV

This example demonstrates the application of a combination of an epoxysiloxane and an aminosiloxane to a fiber from an emulsion.

Part A. 33.3 parts of the epoxysiloxane of Example VI are dissolved in 33.3 parts of isopropyl alcohol and the resulting solution poured slowly into a solution of 1.7 parts of the emulsifying agent stearylcolamino (formyl)methyl pyridinium chloride in 600 parts of water with stirring.

Part B. 16.7 parts of the aminosiloxane of Example II are dissolved in 16.7 parts isopropyl alcohol and the resulting solution poured with stirring into a solution of 0.8 parts of the above-emulsifying agent in 300 parts water.

Parts A and B are thoroughly mixed and immediately applied to a tow of an acrylonitrile polymer fiber comprising a terpolymer of 88.8 parts of acrylonitrile, 5.8 parts of methyl acrylate, and 5.4 parts of 2-methyl-5-vinyl pyridine so as to leave 2% of the total siloxane on the fiber, based on the dry weight of the fiber. This tow is then cut into staple and heated 30 minutes at 130° C. to bring about the reaction between the amino groups and the epoxy groups. The staple fiber is decidedly softer and slicker than an untreated fiber.

Seventy-seven parts of this staple fiber are blended with 33 parts of a staple fiber of the same chemical composition but having been broken on an apparatus, described in U.S. Patent 2,748,426, for stretch-breaking tow into staple fiber (manufactured and sold under the tradename "Turbo Stapler" by the Turbo Machine Co. of Lansdale, Pa.—"Turbo" is a registered Trade Mark) to give a high shrinkage of over 30%. The blended fibers are next spun into a 6/cc (886 denier) yarn with 5Z turns per inch (1.97 turns per cm.). This yarn is two-ply, wound into skeins and dyed with acid colors at a pH of 2.5. The dyed yarn is knit into a two-color welt construction. The fabric possesses a durable, soft, slick hand.

Example V

Into a 2-inch (5.08 cm.) pipeline mixer (commercially available as a Gifford-Wood pipeline homomixer) is fed a mixture of 1870 parts of water, 67.6 parts of the polyepoxide of Example I, 338 parts of the aminosiloxane of Example II, and 7.2 parts of a surface active agent comprising a polyoxyalkylene derivative of a secondary alcohol (commercially available surface active agent identified as Tergitol 13—S—12—"Tergitol" is a registered Trade Mark). The resulting dispersion is pumped continuously onto a moving tow of 450,000 denier of an acrylonitrile polymer fiber comprising a terpolymer of 88.8 parts of acrylonitrile, 5.8 parts of methyl acrylate, and 5.4 parts of 2-methyl-5-vinylpyridine. The tow is dried and cured continuously by passing through an oven at a rate to provide 8.2 minutes residence in an environment at 135° C. The tow is cut into staple fibers 3 inches long and the staple is scoured for one hour at the boil in a 0.5% aqueous solution of a commercially available surfactant (identified as Igepal® CO—880) acidified to a pH of 2.5 with sulfuric acid. The staple fibers are rinsed and dried. A plot is prepared of the coefficient of friction of the fibers, with respect to the sliding speed at which the measurement is made. This coefficient of friction plot is shown in Figure 1. The Objective Preference Index of this fiber, calculated as hereinbefore described, is 0.94.

Similar plots of the coefficient of friction, with respect to the sliding speed at which the measurement is made, are prepared and the corresponding Objective Preference Indexes are calculated for the following fibers: an untreated sample of the same acrylonitrile polymer staple fiber employed in the above paragraph; a commercially available sample of alpaca fiber; a commercially available sample of mohair fiber; an acrylonitrile polymer staple fiber bearing a cured coating of epoxysilicone and 1,4-diaminobutane, prepared as described below; and an acrylonitrile polymer staple fiber bearing a cured coating of a silicone containing silyl hydrogen atoms mixed in admixture with a soluble polyepoxide, and analyzing 2.06% silicone. The Objective Preference Indexes calculated for these fibers are given in Table 1, the fibers being listed in the same order described. The curves for all of these fibers are shown in Figure 2. It will be noted that the fiber of the invention, bearing the cured aminosiloxane-epoxy coating, is very similar in shape to the curves obtained with the natural alpaca and mohair fibers, in that the initial coefficient of friction is relatively low and dips slightly lower to a minimum as the sliding speed is increased, then rises very sharply and progressively as the sliding speed is further increased. The untreated acrylonitrile polymer staple fiber has a high initial coefficient of friction

which decreases somewhat as the sliding speed is increased. The acrylonitrile polymer staple fibers bearing cured coatings of other silicones have low initial coefficients of friction as contrasted with the untreated acrylonitrile polymer staple fibers; but the curves do not rise as the sliding speed increases, so that the coefficients of friction are low regardless of speed.

TABLE 1

Fiber Composition: Cured Coating		OPI
Acrylonitrile Polymer:	Aminosiloxane-epoxy	0.94
Acrylonitrile Polymer:	None (Control)	0.12
Alpaca:	None (control)	0.57
Mohair:	None (control)	1.03
Acrylonitrile Polymer:	Epoxy silicone-1,4-diaminobutane	0.0
Acrylonitrile Polymer:	Silyl hydrogen silicone polyepoxide	0.07

The next-to-last item in Table 1 is prepared by applying a mixture of 4 cc. of 0.40 g. of a dimethyl polysiloxane having 1% pendant epoxide groups and a viscosity of 4000—8000 centistokes in 40 cc. of benzene and 4 cc. of a solution of 0.01 g. of 1,4-diaminobutane in 40 cc. of benzene to 2.0 g. of a 9 denier per filament, 3-inch staple fiber of the same acrylonitrile polymer described in the first paragraph of this example. After evaporation of the solvent, the staple is cured 15 minutes at 135° C. and then scoured one hour at the boil as in the first paragraph of this example, rinsed, and dried.

Example VI

Solutions of the following materials are made in 40 cc. of benzene:

- (A) 0.32 g. of the aminosiloxane described in Example II
- (B) 0.28 g. of the aminosiloxane described in Example II
- (C) 0.24 g. of the aminosiloxane described in Example II
- (D) 0.08 g. of the polyepoxide of Example I
- (E) 0.12 g. 1,3-bis-(3-glycidoxypropyl)tetramethyldisiloxane
- (F) 0.16 g. resorcinol diglycidyl ether

To 2 g. of unmodified 9 denier per filament staple fibers of a terpolymer comprising 88.8 parts acrylonitrile, 5.8 parts methyl acrylate, and 5.4 parts of 2-methyl-5-vinylpyridine in a beaker is added a mixture of 4 cc. of solution (A) and 4 cc. of solution (D) above, and the mass of fibers is worked to distribute the applied solution as evenly as possible. The benzene is allowed to evaporate at room temperature, and the sample is then cured 15 minutes at 135° C. in a forced draft oven. The procedure is repeated for a mixture of solution (B) and solution (E); and repeated again for a mixture of solution (C) and solution (F). Each of the samples of cured fibers is then scoured at the boil for one hour in a solution of 0.5% of a commercially available surfactant (identified as Igepal® CO—880) acidified to a pH of 2.5 with sulfuric acid. After thorough rinsing, the samples are dried at room temperature and their frictional characteristics are evaluated by calculation of Objective Preference Indexes. The results are given in Table 2.

TABLE 2

Epoxy Crosslinking Agent		OPI
	None (no coating)	0.12
	1,3-bis-(3-glycidoxypropyl)tetramethyldisiloxane	0.64
	Resorcinol diglycidyl ether	0.78
	Polyepoxide of Example I	0.89

Example VII

An aqueous dispersion of a coating composition is prepared from 163.4 g. of water, 0.6 g. of a commercially available dispersing agent (identified as Tergitol® 15—S—12), 6.0 g. of the polyepoxide of Example I, and 30.0 g. of the aminosiloxane described in Example II. These ingredients are added in the order listed into a commercially available blending apparatus (Waring Blendor) and are agitated at high speed until emulsified (approximately 3 minutes). The resulting emulsion is diluted to 0.66% silicone with water and applied to untreated 9 denier per filament staple fibers of a terpolymer comprising 88.8 parts acrylonitrile polymer, 5.8 parts methyl acrylate, and 5.4 parts of 2-methyl-5-vinylpyridine to give a 2% coating on the fibers. The fibers are mixed thoroughly in a beaker, and the wet, coated staple is then dried and cured in a forced draft oven at 135° C. for 15 minutes. The cured fibers are then scoured at the boil for one hour in a solution of 0.5% of a commercially available detergent (identified as Igepal® CO—880) acidified to a pH of 2.5 with sulfuric acid.

The procedure described in the preceding paragraph provides a fiber having a cured coating containing 20% of the polyepoxide crosslinking agent, based on the weight of the aminosilicone. This procedure is repeated, employing various proportions of the ingredients, and the frictional characteristics of the fibers are evaluated by calculation of Objective Preference Indexes. The results are given in Table 3.

TABLE 3

Weight Aminosilicone	Weight Polyepoxide (g.)	% Polyepoxide	OPI
33.0 g.	3.0 g.	9	0.89
30.0	6.0	20	0.97
27.0	9.0	33	0.79
24.0	12.0	50	0.81

Example VIII

Solutions of the polyepoxide of Example I in various amounts, as shown in Table 4, are made up in 40 cc. of benzene each. A solution of 0.32 g. of the aminosiloxane of Example II having an amine content of 1.8% in 40 cc. of benzene is also prepared, together with similar 40 cc. benzene solutions of aminosiloxanes having amine contents of 0.4%, 1.0% and 6.0% (aminosiloxanes supplied by Union Carbide Corp., designated Y—6165, Y—5477, and Y—5078 respectively) as shown in the table and in the amounts indicated therein. Mixtures of 4 cc. of the aminosiloxane solutions with 4 cc. of the corresponding polyepoxide solutions are applied to 2.0 g. portions of untreated 9-denier per filament staple fibers of a terpolymer comprising 88.8 parts of acrylonitrile, 5.8 parts of methyl acrylate, and 5.4 parts of 2-methyl-5-vinylpyridine. The fibers are mixed thoroughly in a beaker, and the wet, coated staple is then dried, cured, and scoured as in Example XV. The frictional characteristics of the fibers are evaluated by calculation of Objective Preference Indexes, and the results are given in Table 4.

TABLE 4

% Amine in Aminosiloxane	Wt. of Aminosiloxane	Wt. of Epoxide	% Poly-Epoxide*	OPI
0.4	0.38 g.	0.02 g.	5	0.32
1.0	0.36	0.04	10	0.38
1.8	0.32	0.08	20	0.92
6.0	0.22	0.18	45	0.16

*Based on total weight of coating

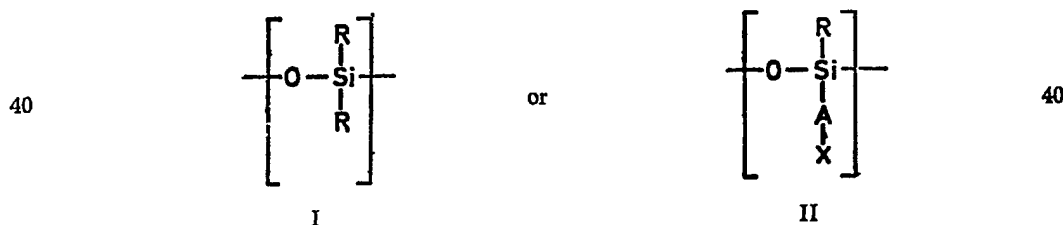
The fiber having the coating containing 6.0% amine and 45% polyepoxide, although slicker than unmodified fiber, has a low OPI value and resembles the natural luxury animal fibers less than the other fibers do.

Example IX

5 A mixture of 87.5 g. of the aminosiloxane of Example II and 1.75 g. of a commercially available dispersing agent (identified as Tergitol® 15—S—12) is made and 204 ml. of water is added slowly with vigorous stirring to produce a 30% emulsion of the aminosiloxane in water. To this is added, in order, 9 ml. of glacial acetic acid, 10 17.5 g. of the polyepoxide of Example I and 3189 ml. of water to produce an emulsion containing 2.5% of the aminosiloxane. The emulsion is applied to a 30,000 denier rope of polyethylene terephthalate polymer fiber of 8 denier per filament by dipping the rope into the emulsion and wringing off excess until the emulsion pickup is 20% based on the rope's dry weight. The rope is then crimped in a stuffer-box 15 crimper and dried and heated for eight minutes by passage through a forced-draft oven at 135° C. to cross-link the surface modifier and relax and crystallize the fiber. A textile finish to provide acceptable textile processibility is applied to the dried, cured rope, and the rope is then cut to 4.5-inch staple fiber. The staple analyzes 0.68% aminosiloxane, based on dry fiber weight. The staple is scoured one hour at 20 the boil in a 0.5% aqueous solution of a commercially available surfactant (Igepal® CO—880) acidified to pH 2.5 with sulfuric acid, rinsed, and dried. A control fiber is prepared in the same way except that 20% water is applied in place of 20% amino- 25 siloxane emulsion. The surface modified fiber has an OPI of 1.64, as contrasted with an OPI of 0.40 for the control. The tactile softness and slickness of knit fabrics made using the surface modified fiber is very pleasing to the hand, and similar to the handle of mohair, whereas the fabric knit from the control fiber lacks the mohair-like hand. The friction plots of the treated and untreated polyester fibers of this example are shown in Figure 3.

WHAT WE CLAIM IS:—

1. A process for the treatment of synthetic organic textile fibers including the application to the fibers of a finishing composition containing (1) a mixture of an aminosiloxane wherein each of the amino groups present carries at least one hydrogen atom and a polyepoxide which has at least 2 epoxy groups per molecule and is not substantially cross-linked or (2) a mixture of a liquid epoxysiloxane having an epoxy group content of at least 1% based on the total weight of said epoxysiloxane and a polyamine having at least 2 amino groups per molecule, each of said amino groups carrying at least one hydrogen atom or (3) a mixture of said epoxysiloxane and said aminosiloxane and subsequently curing of the treated fibers.
2. A process as claimed in claim 1 in which the aminosiloxanes or epoxysiloxanes contain at least 35 repeating units of the formulae



where R is an alkyl group containing 1—4 carbon atoms or an aryl group containing 6—9 carbon atoms;

A is an alkylene group having 2 to 5 carbon atoms or an arylene or substituted arylene group having 6 to 10 carbon atoms; and

45 X is the group —CH—CH_2 or —NH—R'

R' being a hydrogen atom, an alkyl group containing 1—4 carbon atoms or an aryl group containing 6—9 carbon atoms;

when X is —NHR' , R' and A being selected so that not more than one aromatic ring is attached directly to the N-atom; when X is —CH—CH_2 , the epoxy group



content of the epoxysilane being at least 1% based on the total weight of the epoxy-silane; the siloxanes containing at least 2 repeating units of formula II.

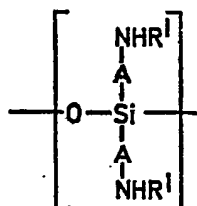
3. A process as claimed in claim 2 in which the aminosiloxane is a liquid.

4. A process as claimed in claim 1 or claim 2 in which the aminosiloxane has no hydrogen atoms bonded to silicon.

5. A process as claimed in claim 2 or claim 3 in which the aminosiloxane or epoxysiloxane contains 100 to 600 repeating units.

6. A process as claimed in claim 5 in which 4 to 20 of the repeating units are of formula II containing the —NHR' group or the —CH—CH_2 group.

7. A process as claimed in any of claims 1 to 6 in which the aminosiloxane contains repeating units of the formula



III

where A and R' are as defined in claim 2.

8. A modification of a process as claimed in any of claims 2 to 7 in which R' alternatively represents a group —A—NHR' where A and R' are as defined in claim 2.

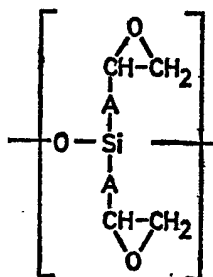
9. A process as claimed in any of claims 1 to 8 in which the amine content of the aminosiloxane is from 0.1 to 5% by weight.

10. A process as claimed in claim 9 in which the amine content is from 1 to 3% by weight.

11. A process as claimed in any of claims 1 to 10 in which the polyepoxide has a molecular weight up to 1000.

12. A process as claimed in any of claims 1 to 11 in which the polyepoxide is water soluble.

13. A process as claimed in any of claims 1 to 12 in which the epoxysiloxane contains repeating units of the formula



where A is as defined in claim 2.

14. A process as claimed in any of claims 1 to 13 in which the epoxysiloxane contains further epoxy groups, provided the epoxy groups are separated from each other and from silicon atoms by at least 2 carbon atoms.

15. A process as claimed in any of claims 1 to 14 in which the ratio of epoxy-siloxane to aminosiloxane is from 0.05:1 to 20:1 by weight.

16. A process as claimed in any of claims 1 to 14 in which the ratio of non-siloxane compounds to siloxane compounds is from 0.05:1 to 3.0:1 by weight.

17. A process as claimed in any of claims 1 to 16 in which the finishing composition comprises a dispersion or solution of the mixture (1), (2) or (3) in an organic solvent or water.

18. A process as claimed in claim 17 in which the solution or dispersion contains 2% to 20% by weight of siloxane.

19. A process as claimed in any of claims 1 to 18 in which the amount of siloxane applied to the fibers is from 0.1% to 3% based on the dry weight of the fibers.

20. A process as claimed in claim 19 in which the amount of siloxane applied is 1 to 2% based on the dry weight of the fibers.

21. A process as claimed in any of claims 17 to 20 in which an aqueous dispersion containing a cationic or nonionic surface active agent is used as finishing composition.

22. A process as claimed in any of claims 1 to 21 in which the finishing composition is applied to a crimped tow of synthetic organic fibers.

23. A process as claimed in any of claims 1 to 22 in which the finishing composition is applied to fibers comprising an acrylonitrile polymer.

24. A process as claimed in any of the preceding claims in which the treated fibers are cured by being subjected to elevated temperatures.

25. A process as claimed in claim 24 in which the fibers are cured at from 110 to 160° C for 15 to 40 minutes.

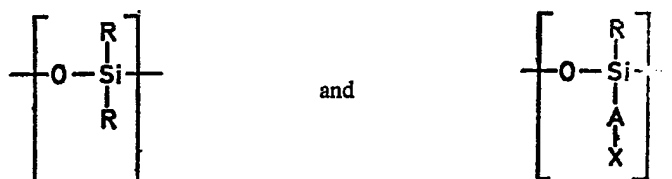
26. A process for treating synthetic organic textile fibers characterized by applying to said fibers a finishing composition and thereafter curing the treated fibers, said composition being

(1) a mixture of 0.05 to 3 parts by weight of an epoxy compound which has at least 2 epoxy groups per molecule and is not substantially cross-linked together with 1 part by weight of a liquid aminosiloxane or

(2) a mixture of 0.3 to 20 parts by weight of a liquid epoxysiloxane together with 1 part by weight of a polyamine having at least 2 amino groups per molecule wherein each of said amino groups has at least one hydrogen atom and not more than one aromatic ring attached directly to the nitrogen; or

(3) a mixture of 0.05 to 20 parts by weight of said epoxysiloxane together with 1 part by weight of said aminosiloxane

wherein the aminosiloxanes or epoxysiloxanes have repeating units of the following formula



wherein

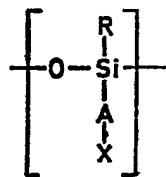
R is an alkyl group containing 1—4 carbon atoms or an aryl group containing 6—9 carbon atoms,

A is an alkylene group having 2 to 5 carbon atoms or an arylene or substituted arylene group having 6 to 10 carbon atoms, X is $-\text{CH}-\text{CH}_2$ or $-\text{NHR}'$

where R' is hydrogen, an alkyl group containing 1—4 carbon atoms or an aryl group containing 6—9 carbon atoms provided in the case of an aminosiloxane.

R' and A are selected so that not more than one aromatic ring is attached directly to the amino nitrogen atom, and provided in the case of an epoxysiloxane that this siloxane has an epoxy group content of at least 1% based on the total weight of such epoxysiloxane

said siloxanes containing at least 35 of said repeating units, at least 2 of which have the formula



27. A process as claimed in claim 1 substantially as herein described.

28. A process for the treatment of synthetic organic textile fibers substantially as herein described in the Examples.

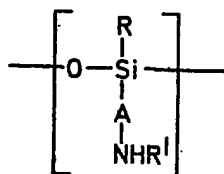
29. Fibers when treated by a process as claimed in any of claims 1 to 28.

30. A treated fiber comprising a synthetic organic textile fiber coated with a cured finishing composition as defined in (1) of claim 1.

31. A treated fiber comprising a synthetic organic textile fiber coated with a cured finishing composition as defined in (2) of claim 1.

5 32. A treated fiber comprising a synthetic organic textile fiber coated with a cured finishing composition as defined in (3) of claim 1. 5

33. A treated fiber as claimed in claim 30 or claim 32 wherein the finishing composition contains anaminosiloxane having 100 to 600 repeating units, 4 to 20 of said units having the formula



10

10

where R, A and R' are as defined in claim 2.

34. A treated fiber as claimed in any of claims 30 to 33 wherein the synthetic organic textile fiber is an acrylonitrile polymer.

15 35. A treated fiber as claimed in any of claims 30 to 32 substantially as herein described. 15

36. The treated fibers herein described in the Examples.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

FIG. 1

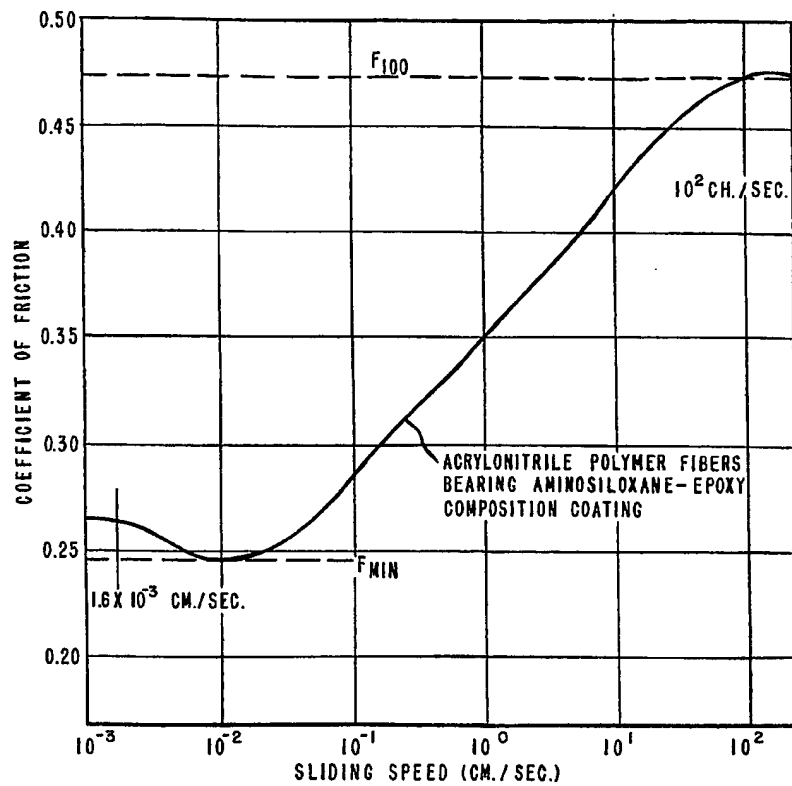


FIG. 2

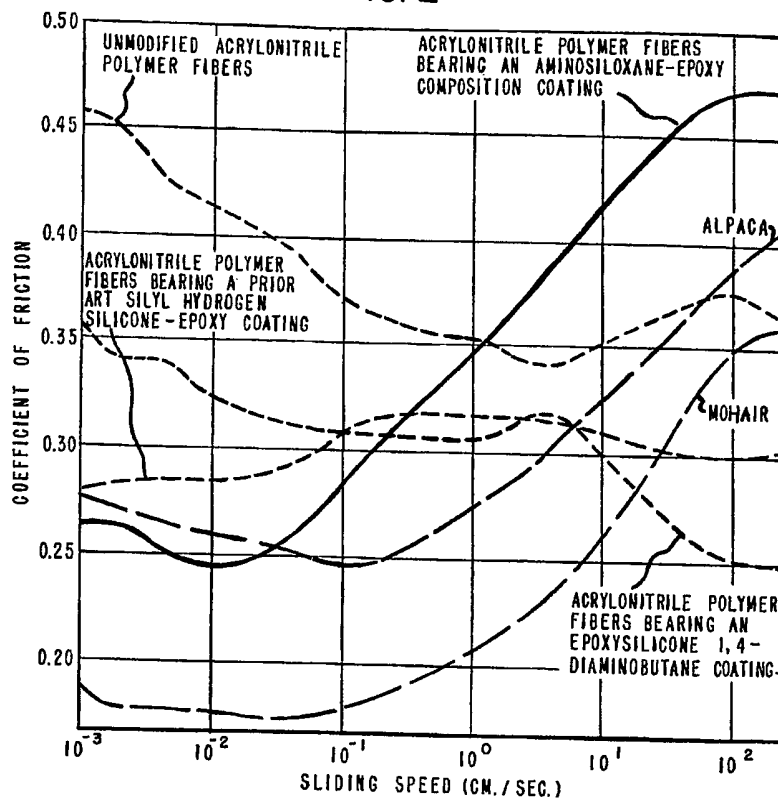


FIG. 3

